

938,040



# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Refractory Materials for use in Converter Linings

We, CANADIAN REFRACTORIES LIMITED, a corporation organized and existing under the laws of Canada, of Canada Cement Building, Phillips Square, Montreal, Province of Quebec, Canada; do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to refractory materials for use in steelmaking vessels, more particularly in the lining of oxygen converters used in the conversion of iron into steel.

It is recognized that the refractory lining of converters and similar vessels, because of the varying chemically reactive character of the charge and the resulting metal and slag, is subjected to extremely corrosive reactive conditions under which there is early attack on the hot face of the lining. The hot slag formed in the converter contains a substantial portion of ferrous oxide which appears to enter and react with the hot face of the refractory lining, making it less refractory and promoting spalling. Moreover, the iron oxide or fluid reaction products tend to migrate inwardly into the lining during continuous or repeated operation of the converter. Both these tendencies cause a progressive deterioration of the lining and greatly decrease its useful life.

The object of the present invention is to provide a refractory composition which resists this progressive tendency in the operation of the converter and thus greatly prolongs the useful life of the refractory lining.

It has been found that when the refractory lining material contains free carbon, the latter has the effect of reducing the iron oxide to metallic iron which will not reduce the refractory character of the lining in the initial or repeated operation of the converter. It has also been found that the relative particle sizes of the major components of the refractory lining material are important in ensuring long life of the lining.

In accordance with the invention there is provided a refractory composition for converter linings, consisting of (a) coarse basic refractory material from the group consisting of dead-burned magnesite containing at least 55% of magnesium oxide and dead-burned dolomite the particles of which are coated with an unbroken layer of calcium ferrite, (b) fine magnesite, which has been burned at a temperature of at least 3000°F, containing at least 55% magnesium oxide, and (c) 2 to 7% by weight of a bonding material, based on the total mix, from the group consisting of tar, pitch and asphalt, the particles of the coarse constituents being all less than 3/8 inch with at least 50% plus 10 mesh, and the fine magnesite being at least 80% minus 65 mesh, the coarse fraction constituting 55 to 80% by weight of the mix. Preferably the coarse fraction constitutes 60 to 75% by weight of the mix.

One of the tests carried out on tars, including those used for bonding, is the determination of "free" or "fixed" carbon. This is the carbon residue left when tested according to an ASTM or other known standard procedure. Generally, in the type of tars used as bonds in accordance with the present invention, this fixed carbon ranges from 13% upwards according to ASTM procedures. Since the term "free carbon" has been used to designate that added over and above the bonding tar, the term "fixed carbon" is used herein to designate the carbon in the bonding tar.

For best results in producing brick, the refractory aggregate and the bonding agent are blended together at a temperature of 200°F. above the softening point of the particular bonding agent used. Experience has shown that 2% to 7% by weight of the bonding medium, based on the total mix, gives a strong brick. After the aggregate and bond have been thoroughly mixed together, the batch is then pressed at a temperature such that the mix will flow into the mould box and

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give maximum density on forming. It has been found that the modulus of rupture of the final moulded product depends to a great extent upon the type and proportion of the binder used, as well as the temperature at which the batch is pressed. Binders having a softening point between 100°F. to 300°F. have been found to be particularly effective.

The mixture may be used in the form of brick or be rammed into place in the converter lining. A suitable batch material using a high melting point pitch as a bond should contain 2—4% by weight of the pitch with 2—4% by weight of oil or creosote as a lubricant.

The presence of carbon in the converter lining, during service, is essential to prevent attack of ferrous oxide. Experience has shown that as the lining is heated in the converter, distillation of the binder back into the colder part of the lining and subsequent carbonization result in a higher percentage of carbon than would normally be found in a brick or the rammed-in-place lining material. Owing to the wide range of conditions to which the lining is subjected the carbon formed in situ, by carbonization of the binder, may vary substantially and not be sufficient to ensure maximum life of the lining. Accordingly up to 7% by weight of finely divided free carbon based on the total mix, may be incorporated in the mix along with the binder to ensure better resistance to ferrous oxide attack.

The finely divided free carbon added, having a particle size not coarser than 100 mesh (Tyler), which mesh standard is employed throughout this description and the appended claims, is one of a group consisting of naturally occurring graphite, manufactured graphite, coke from petroleum or coal, carbon black and pitch. It is well known that high melting point pitches contain a relatively high proportion of non-volatile carbon material which serves the same purpose as graphitic carbon. Thus, when the volatiles are driven off, free carbon is left behind. Pitch is therefore a free carbon-yielding material. Graphitic carbon may be used in an amount between 2 and 5% by weight of the mix. Coke and carbon black are not as desirable as

graphitic carbon because of the tendency to lower density. Also in a mix containing, for example dolomite, which has a tendency to slake readily, the use of coke or carbon black results in a lining less resistant to hydration.

Bonded dolomite brick has been used in the linings of oxygen converters. However, it has been found that additions of fine magnesite to the dead-burned dolomite yields brick of improved physical properties which will better withstand the corrosive conditions present in these converters. It has also been found that the addition of finely divided free carbon further improves these properties. This also applies when magnesite is used instead of dead-burned dolomite as the coarse constituents of the mixture.

Deadburned dolomite, as used in refractories, consists of crushed dolomite admixed with iron oxides and burned to very high temperatures, to give a granular product having a thin coating of calcium ferrite. This coating protects the individual grains from hydration at atmospheric moisture and therefore it is important, in order to avoid degradation of products by atmospheric moisture, to utilize only those dolomite grains which have an intact or unbroken layer of calcium ferrite. Similarly, to be hydration-resistant, the magnesite used in refractories should be dead-burned, i.e. should be burned to a temperature of at least 3000°F.

The following examples are illustrative of the refractory composition of the lining material.

#### EXAMPLE 1

% by weight	
40%	—3/8" dead-burned dolomite
25%	—3/16" dead-burned dolomite
35%	—65m magnesite (94% MgO content)

This was mixed with 5% by weight of tar and moulded into brick. Other magnesites may be used provided that they contain not less than 55% MgO. The dolomite was of the type having no broken grains. The screen and chemical analyses of the fine magnesite and of the brick as well as the physical properties of the brick are shown below.

Screen Analysis	% by weight MgO fines	% by weight Brick
+ 3m		8
+ 4m		18
+ 6m		8
+ 10m		14
+ 28m		17.
+ 65m	13	5
Pan	87	30
Chemical Analysis		
SiO <sub>2</sub>	9	2
CaO	23	31
Fe <sub>2</sub> O <sub>3</sub>	7	3
Al <sub>2</sub> O <sub>3</sub>	1	0.5
MgO	60	58.
loss on ignition		5.5
Bulk S.G.		2.91
Wt./c.f.		182 lbs.
Modulus of Rupture		1700 p.s.i.

## EXAMPLE 2

5 For this batch the same dolomite and magnesite were used along with 3% by weight of finely divided graphite and 6% by weight of tar.

In this case the proportions are:

10      20%      —3/8" dolomite  
          50%      —3/16" dolomite

27%      —65 magnesite (94% MgO  
          3%      content)  
               graphite

The dolomite used had substantially the same screen analysis as in Example 1 as did 15 the fine magnesite.

The physical and chemical properties of the brick and the fines were as follows:

Screen Analysis	% by weight Fine Magnesia	% by weight Brick
+ 3m		4
+ 4m		9
+ 6m		4
+ 10m		19
+ 28m		31
+ 65m	13	6
Pan	87	27
<u>Chemical Analysis</u>		
SiO <sub>2</sub>	3	2
CaO	2	35
Fe <sub>2</sub> O <sub>3</sub>	0.5	2.5
Al <sub>2</sub> O <sub>3</sub>	0.5	1
MgO	94	51
loss on ignition		8.5
Wt./c.f.		182 lbs.
Modulus of Rupture		1200 p.s.i.

Again the dolomite was composed of unbroken grains.

#### EXAMPLE 3

- 5 A special low-silica, high-lime clinker was used for this batch along with fine magnesite of 90% MgO content. Bonding was done with 5.5% by weight of a tar. The batch composition is as follows:

% by weight		
40%	—4 + 10m high-lime magnesite (34% CaO. 55% MgO)	10
25%	—10 + 28m high-lime magnesite (34% CaO. 55% MgO)	
35%	—65m magnesite (90% MgO content)	15

The brick and fine magnesite had the following properties:

Screen Analysis	% by weight High Lime -4 +10m	% by weight Magnesite -10 +28m	% by weight Fine Magnesite -65m	% by weight Brick
+ 4m	5			2
+ 6m	32			13
+ 8m	27			11
+ 10m	31	9		15
+ 28m	4	54		15
+ 65m	1	16	9	7
- 65m		21	91	37
Chemical Analysis				
SiO <sub>2</sub>	3	3	1	2
CaO	34	34	4	22
Fe <sub>2</sub> O <sub>3</sub>	7	7	4	5
Al <sub>2</sub> O <sub>3</sub>	1	1	1	1
MgO	55	55	90	64
loss on ignition				6
Wt./c.f.				176 lbs.
Modulus of Rupture				1260 p.s.i.

It will be recognized that the high-lime magnesite of this example can be replaced by a magnesite of higher MgO content.

- 5                   EXAMPLE 4
- For this batch, all high grade magnesite was used and was bonded with 3% by weight of tar. 6% by weight of finely divided graphite was added to the mix.
- 10   The mix had the following composition:

% by weight  
60% coarse 92%—MgO magnesia  
34% fine 96%—MgO magnesia  
6% graphite

- 15   The resulting brick had the following properties:

Screen Analysis	% by weight Brick
+ 4m	21
+ 10m	31
+ 28m	8
+ 65m	4
- 65m	36

Chemical Analysis:	% by weight Brick	
% SiO <sub>2</sub>	2	25
CaO	3	
Fe <sub>2</sub> O <sub>3</sub>	1	
Al <sub>2</sub> O <sub>3</sub>	1	
MgO	84	
loss on ignition	9	30
Wt./cf.	176 lbs.	
Modulus of Rupture	1830 p.s.i.	

The service life of furnace linings thus made is substantially increased because the rate of consumption of the lining has been reduced. The increase in service life of the lining results in longer periods of operation and consequently fewer shutdowns of the furnace for installation of new linings. This results in the production of more metal per lining installation.

#### WHAT WE CLAIM IS:—

1. A refractory composition for converter linings, consisting of (a) coarse basic refractory material from the group consisting of dead-burned magnesite containing at least

- 55% of magnesium oxide and dead-burned dolomite the particles of which are coated with an unbroken layer of calcium ferrite, (b) fine magnesite, which has been burned at a temperature of at least 3000°F, containing at least 55% magnesium oxide, and (c) 2 to 7% by weight of a bonding material, based on the total mix, from the group consisting of tar pitch and asphalt, the particles of the coarse constituents being all less than 3/8 inch with at least 50% plus 10 mesh, and the fine magnesite being at least 80% minus 65 mesh, the coarse fraction constituting 55 to 80% by weight of the mix.
2. A refractory composition according to claim 1, wherein the bonding material contains at least 13% of fixed carbon.
3. A refractory composition according to claim 1 or 2, containing up to 7% by weight of free carbon based on the total mix, not coarser than 100 mesh and added in the form of at least one of the group consisting of naturally occurring graphite, manufactured graphite, coke, carbon black and pitch.
4. A refractory composition according to claim 1 wherein the coarse fraction constitutes 60 to 75% by weight of the mix.
5. A refractory composition according to claim 3, containing 2 to 5% by weight of carbon in the form of graphite.
6. Refractory composition according to claim 1 substantially as described with reference to the Examples.
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